Proceedings of the American Academy of Arts and Sciences.

Vol. XLVIII. No. 14.—January, 1913.

THE ACTION OF SULPHUR TRIOXIDE ON SILICON TETRACHLORIDE.

By Charles Robert Sanger and Emile Raymond Riegel.

THE ACTION OF SULPHUR TRIOXIDE ON SILICON TETRACHLORIDE.[1]

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Presented by C. L. Jackson, November 13, 1912. Received, October 24, 1912.

The reaction between sulphur trioxide and carbon tetrachloride yields phosgene and pyrosulphuryl chloride.[2]

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$$

Since the two elements carbon and silicon resemble each other so closely, it was reasonable to suppose that a similar reaction might take place if silicon tetrachloride were substituted for the carbon tetrachloride. In order to test this, or to find out what reaction, if any, took place, this research was undertaken.

The only reference to the subject we can find in the literature is the following note of Gustavson, quoted in extenso:

"Silicon tetrachloride gives with sulphur trioxide pyrosulphuryl chloride." [3]

This information Dammer [4] enlarges into the following reaction:

$$4SO_3 + SiCl_4 = 2S_2O_5Cl_2 + SiO_2$$

Our investigation showed that on mixing pure melted sulphur trioxide and silicon tetrachloride, there is at first mere solution, but on standing, a reaction takes place, exceedingly slowly in the cold, but more rapidly at about 50°, resulting in the formation of a liquid which when freed by distillation from the unchanged materials boils between 135° and 150° at atmospheric pressure, whereas sulphur trioxide and silicon tetrachloride boil below 60°. This distillate fumes weakly in

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1 This research was suggested by the late Professor C. R. Sanger and most of the work was done under his direction, until he was prevented by illness from continuing its supervision, when Professor T. W. Richards took charge of it. The material was prepared for publication with the aid of Professor C. L. Jackson after the lamented death of Professor Sanger, who is therefore in no way responsible for its arrangement or presentation. I am very grateful to Professors Richards and Jackson for their respective aid. E. R. R.

The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy by Emile Raymond Riegel.

2 If water is present, a certain amount of chlosulphonic acid is formed, very nearly proportional to the quantity of water. See Sanger and Riegel, These Proceedings, **47**, 673 (1912); Zeit. anorg. Chem., p. 79 (1912).

3 Ber., 1872, **5**, 332.

4 Dammer, Inorg. Chem. **1**, 667.

moist air and reacts violently with water; it contains sulphur, chlorine, silicon, and oxygen, and the indefiniteness of its boiling point indicates that it is a mixture. We have not succeeded in isolating the substances of which it is composed, although we tried every way we could devise. Nevertheless we are convinced that it is made up of pyrosulphuryl chloride $S_2O_5Cl_2$ and silicon oxychloride Si_2OCl_6, because all our complete analyses of well-established specimens give percentages corresponding to such a mixture; that is, if the amount of sulphur found is assumed to be present as pyrosulphuryl chloride, and the amount of chlorine corresponding to the sulphur in that compound is calculated, the difference between the total chlorine and this amount agrees well with the chlorine necessary to form silicon oxychloride with the silicon found; thus out of 18 analyses, it agrees in 8 cases within 1 percent, in 5 other cases within 2 percent, in one more case within 2.5 percent. The four remaining analyses gave results which did not agree, but this is satisfactorily explained, for these are analyses of fractions boiling at higher temperatures than the usual one, namely above 150°, indicating the presence of other substances. These analytical results are confirmed by other observations. A specimen distilled from a heavy gelatinous residue of silicic acid gave results on analysis differing by only 1.8 percent on the sulphur, and 4 percent on the chlorine from pyrosulphuryl chloride, showing that that substance had been formed; another distilled from a large excess of phosphorus pentoxide, melted at $-40°$ to $-50°$ and crystallized in radiating crystals like pyrosulphuryl chloride which melts at $-37°$, showing its presence again; a third, distilled from an excess of sodium chloride gave analytical results indicating a more impure pyrosulphuryl chloride. It seems therefore that heating the liquid with a large excess of any solid disposes of most of the silicon oxychloride, but reveals the presence of the pyrosulphuryl chloride.

The boiling point of the distillate, 135–150°, is what would be expected of a mixture of pyrosulphuryl chloride and silicon oxychloride, for the former boils at 152.5°–153°, and its boiling-point may be lowered 5–10° by a minute amount of water, and the latter boils at 136–139°. The boiling-point of the mixture is not changed by the addition of one fifth of its weight of pyrosulphuryl chloride. If a great deal of water is added to the original distillate a violent reaction attended with the formation of silicic acid takes place such as would be expected from silicon oxychloride and a heavy liquid separates at the bottom of the vessel, dissolving but slowly. This is the behavior of pyrosulphuryl chloride or of sulphuryl chloride, but the latter is excluded by the

boiling point of the mixture, hence it must be the former. Chlorsulphonic acid, the only other compound of sulphur which might be expected, and then only in those preparations in which hydrous sulphur trioxide was used, was found to be absent by a distillation with salt, when only a very small amount of hydrochloric acid was given off.

It appears from these observations that silicon tetrachloride does not behave like carbon tetrachloride with sulphur trioxide, the principal reaction being represented as follows:

$$2SO_3 + 2SiCl_4 = S_2O_5Cl_2 + Si_2OCl_6 \quad (1)$$

If it did behave like carbon tetrachloride, the reaction would be:

$$2SO_3 + SiCl_4 = S_2O_5Cl_2 + SiOCl_2.$$

We base our contention that $SiOCl_2$, the unknown oxychloride of silicon which would be analogous to phosgene, and might therefore be called silico-phosgene, is not formed on the fact that all the properties of the silicon compound resulting from the reactions point to the oxychloride, Si_2OCl_6; furthermore, on the analyses, and on our failure to find the silico-phosgene in the lower boiling fraction, where it would be expected. The liquid distilled from the reaction mixture below 130° gave on distillation sulphur trioxide vapors, a mixture of sulphur trioxide and silicon-tetrachloride, an almost pure silicon tetrachloride which was on several occasions re-distilled and found to boil at 56–58°, its true boiling point being 57°, and a little of the higher boiling fraction. In the distillation in vacuo, a vessel cooled with liquid air was added to condense any silico-phosgene, but nothing was found there beyond silicon tetrachloride and sulphur trioxide. The weights of the various condensations and residues were always noted; their nature being established as either unchanged substances, or as the mixture of oxychloride and pyrosulphuryl chloride, nearly all the material was accounted for (thus in one case 94%), so that no considerable amount was left which might have formed the silico-phosgene. In nearly everyone of the twenty-six preparations made the proportions taken were those of two molecules of sulphur trioxide to one of silicon tetrachloride, favoring the reaction $2SO_3 + SiCl_4 = SiOCl_2 + S_2O_5Cl_2$; nevertheless every fact points to the formation of silicon oxychloride, and none to that of silico-phosgene. That silico-phosgene is unknown also speaks against the likelihood of its formation in this reaction.

In three cases distillates were obtained which were not very far removed from a mixture of the two products in molecular proportions, as required by reaction (1), but in most cases there was a decided excess

of the pyrosulphuryl chloride, especially if the preparation had been allowed to stand some time, in one case three summer months. This excess may be formed by the following reaction:

$$Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5Cl_2 \quad (2)$$

as a considerable amount of silica is deposited during the standing.

It follows from our work that the reaction constructed by Dammer on Gustavson's meagre statement

$$4SO_3 + SiCl_4 = 2S_2O_5Cl_2 + SiO_2$$

is incorrect, inasmuch as there is formed at first the oxychloride:

$$2SO_3 + 2SiCl_4 = S_2O_5Cl_2 + Si_2OCl_6 \quad (1)$$

and only by a secondary reaction, silica,

$$Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5\,Cl_2$$

By combining the two reactions that given by Dammer is indeed obtained, but (2) takes place only to a limited extent and always follows (1). To give Dammer's equation alone would be misleading; the two separate equations (1) and (2) must be given and explained.

There is some evidence that the distillate contains a loose compound of pyrosulphuryl chloride, $S_2O_5Cl_2$, and silicon oxychloride, Si_2OCl_6, formed under the influence of heat. The distillate did not freeze unaided above $-78°$, except in a single case, while a mixture of equal parts of the two substances crystallized easily on cooling and melted at $-40°$ to $-38°$. It is astonishing that this mixture melted at about the same temperature as its constituents, $S_2O_5Cl_2$, melting at $-37°$, Si_2OCl_6 at $-40°$. A mixture of 15.6 grams of $S_2O_5Cl_2$ with 5.2 grams Si_2OCl_6, which therefore had about the same composition as one of our distillates crystallizing at $-78°$, was divided into two parts, one of which was heated for 5 minutes in the Bunsen flame; on cooling the two in the carbon dioxide-alcohol mixture, the portion which had been heated took 20 times as long to begin to solidify as the unheated one. This could hardly be accounted for unless the supposition was made that the two substances had combined under the influence of heat. The assumption of such a compound does not interfere with the other observations made, thus the boiling point might remain that of mixed silicon oxychloride and pyrosulphuryl chloride, because the compound between the two is too weak to exist in the state of vapor, a recombination, however, taking place as they return to the liquid phase; the formation by distillation of nearly pure pyrosulphuryl chloride took place only when the temperature was raised much higher than usual,

so that the compound would be decomposed, the silicon oxychloride disappearing completely as such, leaving the pyrosulphuryl chloride; again the reaction of water on such a compound might well be a decomposition into the components accompanied by the destruction of the silicon oxychloride, leaving a part at least of the pyrosulphuryl chloride to react more slowly, for it is less sensitive to water than the oxychloride, as shown quantitatively further on. It must be added, however, that all the distillate which gave distinctly the oily deposit with water were low in silicon, and contained an excess of pyrosulphuryl chloride, so that all of the combined oxychloride and pyrosulphuryl chloride might have been destroyed, leaving only the free pyrosulphuryl chloride to become visible. The assumption of this compound explains to perfection why the distillates nearing in percentage composition an equi-molecular mixture of the two substances did not crystallize even after seeding with pyrosulphuryl chloride, while the distillates low in silicon, containing an excess of pyrosulphuryl chloride, which could exist free, crystallized readily under the same conditions. Reaction (2) is not affected by this assumption, for it takes place on standing at room temperature, or at the most at 50°, so that the loose compound, for which we assume that a temperature of about 130° is needed, is not formed. Our effort, however, was to prove reactions (1) and (2) rather than study this subsequent compound.

EXPERIMENTAL PART.

Materials: The commercial sulphur trioxide marked C. P. contained no impurities. In order to obtain a liquid at room temperature it was melted for some experiments, for others the melted substance was added to fuming sulphuric acid in the proportions necessary to give solutions of various strengths which were ascertained by titration or gravimetrically. The melting was done in a cylindrical copper air bath built for the purpose, and this was extraordinarily easy with a fresh sample;[5] a moderate temperature was required (about 50° in bath), the melting was rapid, no clots formed in the center, and the low temperature caused little boiling, hence little pressure, so that the stopper could be left in place without danger; with an old sample on the other hand the melting was almost impossible; so much heat was

[5] Fresh sulphur trioxide melts at 17.7°; old samples do not melt at all, but sublime; Knietsch, Ber., **34**, 4101 (1901). Compare also Schenck, Lieb. Ann. **316**, 1 (1901); Weber, Ber., **19**, 3187 (1886).

needed that the small quantity which had melted boiled away before any more became liquid.

Silicon tetrachloride was prepared by passing dry chlorine over powdered silicon spread out in a hard glass tube, and heated in a combustion furnace.[6] An adapter at the end of the tube (the latter was slightly inclined towards the former) fitting into a receiver set in ice, completed the apparatus. Charges of 50 grams yielded 190 to 225 grams of silicon tetrachloride, that is, 64 to 75 percent of the theoretical yield. Special effort to obtain a large yield was never made; on the contrary economy of time was the only consideration. In this respect this method is ideal; the apparatus could be set up in a few minutes, and a preparation carried through in an afternoon.[7] The silicon contained iron, which caused the presence of ferric chloride in the crude product; the latter also contained free chlorine. The crude product was freed from chlorine by shaking with mercury and was then distilled.[8] It was kept in glass stoppered bottles under a dry bell-jar, or the flasks were sealed off. The bottles were left in the open at first, but the moist air caused a deposit of silica which cemented the stopper in place, and such a bottle could only be opened by breaking it, when it usually exploded. Rubber stoppers were found more satisfactory, but these hardened in time and also became cemented. Bottles nearly empty and imperfectly closed to moisture exploded spontaneously, because of the formation of hydrochloric acid.

Silicon oxychloride was prepared by the method of Troost and Hautefeuille[9], namely, by passing a mixture of chlorine and oxygen over heated metallic silicon in the same apparatus as the one used for silicon tetrachloride. The yield was very small; out of 154 grams a

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6 Hempel and Haasy state that they used this method, but give no details. Zeitschr. anorg. Chem., **23**, 32 (1900).

7 In our earlier work the silicon tetrachloride was made by passing chlorine over silicide of copper as done by G. H. Pratt (M. I. T. thesis, 1897, vol. 68; in the hands of Vigouroux, C. R., **129**, 334 (1899), this method did not give satisfactory results) except that glass retorts were used instead of iron tubes, but this method was much slower, less convenient, and gave a poor yield.

8 The melting point of silicon tetrachloride is −69° (corr.) It was determined several times on different samples, by the beaker method (see note 11) and by complete immersion of the thermometer. W. Becker and J. Meyer (Zeitschr. anorg. Chem. **43**, 251 (1905)) give this point as −89°; they determined it by winding a thermo-element on the outside of the containing vessel, while this was suspended in a Dewar tube containing a little liquid air; the junction was presumably at the bottom of the containing tube. Their material was exceedingly pure, but the method used in obtaining the melting-point is open to objection.

9 Bull. Soc. Chim., **35**, 360 (1881).

yield of 5.5 grams of the oxychloride Si_2OCl_6 was obtained, after several fractionations. The greater part of the crude material was silicon tetrachloride, besides some 35 grams of the higher oxychlorides. The method was nevertheless better than that of Friedel and Ladenburg [10], from which we obtained absolutely no yield. These five grams were found to crystallize readily, melting at $-41°$ to $-38°$, corr. by the beaker method.[11]

Analyses: Rapid analyses for chlorine and sulphur were made volumetrically. A small bulb containing a known weight was broken in water; the solution made up to a definite volume and aliquot portions used. As a rule part of the silica precipitated. The total acidity was found by titrating against standard potassium hydroxide. The effect of the silicic acid on the indicator (phenol phthalein) was not to be considered, as the method was intended merely for following changes in whole percentages. The chlorine was determined by the Volhard method, with which the silver silicate does not interfere, for it is readily decomposed by all strong acids.[12] The acidity and the chlorine content were expressed in terms of a normal solution; from the difference the percentage of sulphur was calculated.

The accurate determinations were made as follows:

Silicon and Sulphur: A bulb containing a known weight was broken in a freshly prepared solution of sodium hydroxide made from sodium, and which had been shown to contain no silica, chlorine, or sulphur. The solution was filtered from the pieces of glass into a platinum dish, and acidified with sulphate-free hydrochloric acid.[13] The analysis

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10 Lieb. Ann., **147**, 355 (1868); C. R. (1868) **66**, 539; also Troost and Hautefeuille, C. R. (1871) **73**, 563; J. prakt. Chem., (2) **4**, 304 (1871).

11 A rapid method for obtaining melting-points at low temperatures was used. A small melting-point tube, as used in organic work, contains the substance already crystallized by dipping it in liquid air; this is placed in a beaker containing naphtha which has been cooled by immersion in liquid air also. By removing the latter, the bath is permitted to warm up until the substance melts; the temperature is read on a pentane thermometer calibrated in the same way as it is used. A full description will be found in a previous article, Proc. Am. Acad., **47**, p. 699. It will be called the "beaker" method.

In addition to this method the "immersion" method, in which the thermometer is placed in the melting substance, after having been standardized for that use, was employed whenever possible.

12 J. D. Hawkins, Am. Jour. Sc., **139**, 311 (1890).

13 The time during which the alkaline solution was in contact with glass varied between twelve and twenty-five minutes. In order to show that no glass was dissolved, the pieces of glass from one of the bulbs were collected, after the alkaline solution had been removed, and weighed:

Glass recovered 0.7458 gram.
" taken 0.7452 gram.

was continued in the customary way, involving in the earlier analyses two evaporations with intermediate filtrations, and corrections with hydrofluoric acid, but these corrections were found to be so small that the accuracy desired did not justify the work necessitated by them. Later therefore only one filtration was made, and the hydrofluoric acid correction left out. In the filtrate from the silica, the sulphur was determined as barium sulphate.

Chlorine: A bulb containing a known weight was broken in a solution of the sodium hydroxide. The liquid was filtered into a precipitating flask, and, after adding a drop of phenol phthalein, weakly acidified with chlorine-free nitric acid; silver chloride was precipitated from the clear solution, and weighed on a Gooch crucible.

In order to determine how much silica was carried down by the precipitate, a sample of silicon tetrachloride was treated with sodium hydrate, and the alkaline solution evaporated in a platinum dish; the silica was removed, and the chlorine determined. It was found to be 83.3 percent. The same material was then analyzed without removing the silica and there was found 83.6 percent of chlorine. Several other determinations confirmed this result. The amount of inclusion depends mainly upon the dilution at the moment of precipitation, and upon the percentage of silicon in the substance. The dilution was always made considerable, and while silicon tetrachloride contains 16.63 percent of silicon, the material analyzed contained one half to one fourth as much. Therefore it seemed safe to assume that the analyses had an accuracy of 3 parts in 1000, or 0.3 percent, which satisfied the requirement in this work.

The Mixtures.

When sulphur trioxide was added to silicon tetrachloride they mixed at once forming at 32° a clear colorless liquid, which after being sealed and standing in the room deposited long white needles like those of sulphur trioxide from which we inferred little or no reaction had taken place, but after this liquid had been heated in an air bath to 50° for 6 hours a reaction took place as shown by the formation of a product boiling between 135° and 150° at atmospheric pressure, whereas sulphur trioxide boils at 46° and silicon tetrachloride at 57°. A considerable deposit of silica also appeared in many of our experiments.[14]

14 Preliminary experiments tried by Mr. Maurice L. McCarthy led to the formation of distillates similar to those described later.

Solid sulphur trioxide did not dissolve in silicon tetrachloride and liquid mixtures of the trioxide and fuming sulphuric acid containing 8 percent of water or less, did not mix with the tetrachloride, but such hydrous sulphur trioxide solutions were made to react with it by shaking the two for several hours (5½ to 12) at room temperature, or better still by directing a blast of air warmed to 50°, on the bottle while on the shaker, when the mixing took place in less than an hour. The product after distillation could not be distinguished from that obtained from pure melted sulphur trioxide, except on analysis, when the former was found to contain roughly 14 percent sulphur, the latter 21 percent, and on cooling and seeding with pyrosulphuryl chloride, the latter could be made to crystallize, but not the former. The reason is self-evident, for in the former cases the water was combined with much of the sulphur trioxide, reducing its concentration as such; in the latter, the concentrations remained high, and reaction (2) could take place to a sufficient extent to raise the amount of pyrosulphuryl chloride. The yield (50 percent in the best case) seemed to be better when no water had been used in the sulphur trioxide, and when the proportions were those of two molecules of sulphur trioxide to one of silicon tetrachloride; an excess of either reagent diminished the action.

This product was freed from the unaltered reagents by distillation either at atmospheric or at reduced pressure. Its character and our attempts to prepare a pure substance from it are best made evident by the description of two of our most extended experiments.

101 grams of silicon tetrachloride were added to 100 grams of 93.8 percent sulphur trioxide, being 1 molecule of the former to 2 of the latter, and after shaking 5½ hours a pale brown homogeneous liquid was formed which on standing over night deposited a flocculent precipitate and became colorless. 145 grams of the supernatant liquid were distilled at 16 mm. pressure with two condensers inserted between the receiver and the pump; the first was cooled by solid carbon dioxide mixed with absolute alcohol, and was destined to collect sulphur trioxide and silicon tetrachloride; the second was cooled by liquid air, and could therefore condense hydrochloric acid besides any material escaping the first tube.[15] 76 grams were collected at 42° to 70°. The tube at −78° contained 9 grams, the liquid air tube. 19.5 grams. These were silicon tetrachloride and sulphur trioxide In the subsequent distillations a single condenser cooled by liquid air

[15] For description of the kind of tube used in the liquid air, see Sanger and Riegel, These Proceedings, **47**, 697.

was used. A hard residue which weighed 32 grams, was left in the boiling flask.

The 76 grams were distilled again. The material condensed by the liquid air was 1.7 percent of the weight taken, the residue in the flask also 1.7 percent. The 72 grams collected were distilled once more; 70.7 grams were obtained. In this third distillation, the more volatile matter was less than 0.15 percent, the hard residue in flask 0.5 percent. The material distilled at 49° to 70° with a pressure of 17 mm.; the highest temperature of the bath was 120°, the time thirty minutes. The distillations showed that the 76 grams contained no silicon tetrachloride, no sulphur trioxide, and no considerable amount of dissolved or suspended silica; an analysis showed the presence of 17.2 % S and 49.3 % Cl; the silica was not determined. No crystals could be formed, but the material congealed at −120°. This behavior suggested impure chlorsulphonic acid; so in order to determine whether it was present or not, 65 grams of the substance were treated with 40 grams of common salt.[16] (22 grams would have been required if all the sulphur found by analysis had been present as chlorsulphonic acid, hence the enormous excess would be expected to retain mechanically a great deal of the liquid). On adding the salt, no bubbling of hydrochloric acid gas occurred, as is always the case with chlorsulphonic acid; a distillation at low pressure gave 43.5 grams of distillate. In the liquid air condenser there were 3 grams of a liquid which were undoubtedly uncondensed distillate and hydrochloric acid. The large distillate, accompanied by the insignificant amount of hydrochloric acid,[17] established the absence of chlorsulphonic acid as an essential part of the liquid. The composition was

	S	Si	Cl
(1)	16.9%	9.4%	53.3%

not markedly different from that of the liquid before treatment with salt. Nevertheless in subsequent mixtures a distillation from salt was frequently performed, in order to remove even the smallest amount of chlorsulphonic acid that might have been formed.

The 43.5 grams were distilled twice more, at low pressure, in an effort to obtain a constant boiling-point, but in neither case was the temperature steady; the best result was the second fraction in the

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16 For this method of removing chlorsulphonic acid, see also Sanger and Riegel, These Proceedings, **47**, 689.

17 A portion of this hydrochloric acid was formed by the action of the vapors on the rubber corks and connections.

second distillation, which weighed 23 grams and boiled from 45.8° to 48.2° at 11–13 mm. This material analyzed gravimetrically contained:

	S	Si	Cl
(2)	14.63%	10.20%	54.87%
(3)	14.50%	10.18%	
$1S_2O_5Cl_2$ $+1Si_2OCl_6$	12.82%	11.31%	56.69%

The composition of an equi-molecular mixture of pyrosulphuryl chloride and silicon oxychloride is given above, and it can be seen that the liquid gives similar figures.

Distilled at atmospheric pressure the temperature rose steadily and evenly from 141° to 150°. No crystals were obtained on cooling. To the distillate one fifth of its weight of pyrosulphuryl chloride was added, and it was then distilled again when the temperature readings were unchanged. On cooling no crystals were formed; the material congealed as before, below −100°.

In our second extended experiment 236 grams of silicon tetrachloride and 221 grams of melted anhydrous sulphur trioxide, that is, one molecule of the former to two of the latter, were heated in the air-bath for six hours at 50° and deposited 8 percent of a white solid. 205 grams of the liquid poured off from this solid were distilled at ordinary pressure and gave

90 grams at 37–44°
62 " " 44–58°
31 " " 59–145°
21 " " residue.

(Sulphur trioxide boils at 46°, silicon tetrachloride at 57°). The third fraction and the residue gave on a second distillation 20 grams at 135–151° and 16 grams at 151–172°; these 20 grams did not crystallize on cooling, and were therefore distilled again, and separated into four fractions. The second one only, 6 grams collected at 137–145° (4, 5) could be made to crystallize at −83°, melting at −50°; the remaining three fractions were combined and distilled, the distillate being collected in 3 portions, the middle one, 138–143° (8, 9) crystallized spontaneously; the lower one, 136–138° (6, 7), on stirring; the upper one, 143–176° (10, 11) only on seeding from the lower one. As none of these fractions showed any signs of constant boiling-point, the crystallization was studied further. For this purpose each fraction was

introduced into a special separator[18], crystallized and the mother liquor drawn off; the crystals were then allowed to melt, drawn off in their turn, and analyzed. Only the fraction 138–143° was not separated into crystals and mother liquor, because its amount was too small.

		S	Si	Cl
(4)	137–145°	21.37%	5.25%	43.68%
(5)		21.33	5.45	43.94
(8)	138–143°	22.88	4.4	41.65
(9)				41.68
(6)	136–138°	21.9	4.9	43.00
(7)		22.0		
(10)	143–174°	22.73	5.28	39.74
(11)		22.89	5.38	
(12)	Mother liquor	22.97	5.19	39.73
(13)	of crystals			39.44

These analyses show that the fractional distillation gives little or no promise of leading to a pure product as the percentages of sulphur and silicon in the different fractions differ by 1.1 percent or less, those of chlorine by 3.56 percent or less Nor is crystallization more promising since there is essentially no difference in composition between the crystals (10, 11) and their mother-liquor (12, 13).

Another preparation similar to the last was allowed to stand for three summer months in a glass stoppered bottle under a bell-jar whose atmosphere was kept dry by phosphorous pentoxide; during this time a solid amounting to 23 percent of the total weight was deposited, and on distillation a fraction of 53 grams or 38 percent boiling at 136–156° was obtained. This fraction when cooled to −78° did not crystallize, but on inoculation with a crystal of pyrosulphuryl chloride it did, so many crystals developing that it became a stiff paste; this had been done in the separator, and after warming a little, the mother liquor was drawn off; the process was repeated twice, the melted crystals serving as starting material each time. After making an analysis (14) of the final crystals, a portion of the original 53 grams was taken and the crystallization was repeated, but this time with an alcohol bath cooled to −65° and −60° instead of −78°, in order to reduce the supercooling. The material was fractionally crystallized 4

[18] Sanger and Riegel, These Proceedings, **47**, 710. It consisted essentially of a glass vessel holding a platinum cone, and connections above and below so that suction might be applied below or above, all out of contact with moist air.

times, with a seed of pyrosulphuryl chloride, the separation taking place in order at −65°, −60°, −60°, and −60°; the crystals thus purified weighed 3.5 grams, and their analysis (15, 16) is given below. The mother liquors were then combined, and a crystallization from a silicon oxychloride seed attempted, but it failed, for only at —78° could crystals be obtained, and at that low temperature, crystallization was spontaneous; nevertheless, the crystallization was repeated twice, and the final crystals analyzed (17). The analysis of the original 53 grams is also given (18).

	S	Si	Cl
(14)	23.98%	3.7 %	40.02%
(15)	24.28	3.78	39.57
(16)	24.03	3.85	39.38
(17)	23.62	4.07	40.08
(18)	23.26	4.90	41.61

The composition had not changed markedly; (14) has more sulphur and less silicon than (18) which would point to a concentration of pyrosulphuryl chloride; the fact that it crystallized at −60° rather than at −78° also supports this assumption, but at −60° the supercooling is still considerable; (15) and (16) differ too little from (14) to have a meaning, so that neither the analysis nor the crystallization with pyrosulphuryl chloride show that all the pyrosulphuryl chloride is present as such. The failure of crystallization with silicon oxychloride is reflected in the analysis (17) which hardly differs from (18) the original material, showing that the silicon oxychloride is not present free.

The experiments described above show why we did not succeed in obtaining a pure substance from our product either by fractional distillation or crystallization; an additional experiment might be mentioned as having led to the same result. A preparation similar to the previous one was fractionally distilled 5 times, at atmospheric pressure, using a dephlegmator, and yielded two fractions boiling over several degrees:

		S	Cl
(26)	145–149°	15.3%	50.6%
(27)	149–157°	17.1	50.7

But in spite of our failure to isolate the pure substances, our analyses established the nature of the two compounds of which this mixture is made up. For this discussion we have collected all the complete analyses already given and all the others made by us in a table. Of

the analyses not already given the product for (19) was made by heating solid sulphur trioxide and silicon tetrachloride in sealed tubes at 250°; when the tubes were opened there was no pressure, showing that no gas was formed by the reaction. A fraction boiling at 135–157° was purified by distilling it at a pressure of 1.5 mm., and a product obtained boiling at that pressure at 29.5° to 34°. A preparation made almost like that of analysis (2) and (3) yielded a lower fraction analyzed under (20) while a higher fraction which approached pyrosulphuryl chloride in composition and behavior will be discussed later. Finally three analyses were made of fractions obtained from a liquid similar to the preceding ones, but which had been treated with water, in order to destroy if possible one of the constituents; one of these fractions (21) was submitted to two distillations at low pressure; another (22) was this preceding product after treatment with salt, in order to remove any chlorsulphonic acid which might have been formed by the action of the water; the third (23) was collected from the same flask, but after the temperature had been raised from 150° to 210°, with the pressure still 20 mm., a degree of superheating almost certain to cause decomposition, since the average boiling-point at such pressures is below 100°. This action of the study of water will be referred to further on.

The percentages of chlorine marked "calculated" in the table were obtained by computing the percentage of chlorine which would correspond to the percentage of silicon in each analysis if this were present as silicon oxychloride, Si_2OCl_6. The amount of chlorine was then calculated which would be combined with the percentage of sulphur if this was present as $S_2O_5Cl_2$, and subtracted from the percentage of chlorine recorded by the analysis and the remainder entered as "Found" in the table.

From this table it would appear that 13 out of the 18 analyses agree within 2 percent, of the calculated amount of chlorine in a mixture of pyrosulphuryl chloride and silicon oxychloride, and one more (18) within $2\frac{1}{2}$ percent; moreover, among these 14, 8 agree within 1 percent. Of the four which do not agree, all were analyses of fractions boiling at higher temperatures than the average, 135–150°; thus (10) and (12) at 143–174°, (22) at 52–110° with a pressure of 20 mm. and (23) over 110° with the same pressure, the oil-bath around the boiling flask being finally at 210°. These high temperatures indicate that impurities were present, as products of decomposition, or substances due to the action of moisture from the air and of organic matter in the shape of unavoidable rubber stoppers; there would seem to be sufficient ground

TABLE OF COMPLETE ANALYSES.

	S	Si	Cl	Cl Calculated	Cl Found
(1)	16.9%	9.4%	53.3%	35.3%	34.6%
(2)	14.63	10.20	54.87	38.34	38.69
(4)	21.37	5.25	43.68	19.73	20.05
(5)	21.33	5.45	43.94	20.49	20.35
(6)	21.9	4.9	43.00	18.42	18.78
(8)	22.88	4.4	41.65	16.54	16.35
(10)	22.73	5.28	39.74	19.85	14.60
(12)	22.97	5.19	39.73	19.51	14.33
(14)	23.98	3.7	40.02	13.9	14.5
(15)	24.28	3.78	39.57	14.21	12.72
(16)	24.03	3.85	39.38	14.47	12.80
(17)	23.62	4.07	40.08	15.30	13.86
(18)	23.26	4.90	41.61	18.42	15.89
(19)	15.14	10.14	53.15	38.12	36.41
(20)	19.6	6.3	45.2	23.7	24.5
(21)	20.1	6.1	43.4	22.9	21.2
(22)	19.9	6.75	43.4	25.4	21.4
(23)	24.2	3.9	35.2	14.7	8.4

for excluding them, and if this is done, all the complete analyses of the well-established specimens of the mixture show that it is made up of pyrosulphuryl chloride and silicon oxychloride only. This inference is confirmed in a number of different ways.

The boiling-point of this fraction 135–150° is what would be expected for while pyrosulphuryl chloride boils at 152.5–153°, the least trace of moisture causes a considerable portion of it to boil 5° to 10° lower, and the boiling point of silicon oxychloride is 136–139°.[9]

The behavior of the distillate with water also is a valuable indication. When much water was added to it there was a violent reaction accompanied by the formation of silica, such as silicon oxychloride gives, and an oily liquid separated and sank to the bottom of the vessel, where it dissolved very slowly, showing the behavior of pyrosulphuryl chloride; dilute sodic hydrate acted in the same way. As described before, the crystallization could be induced with a com-

paratively moderate degree of cooling below its freezing-point by a crystal of pyrosulphuryl chloride in those mixtures which had 5 per-cent or less of silicon, and the crystals obtained in this way gave an analysis indicating a concentration of pyrosulphuryl chloride (14) compared with (18), the mother liquor. Finally several distillates were obtained under certain conditions stated further on, which were almost pure pyrosulphuryl chloride; these cannot be used as proof of its presence because they were obtained at temperatures higher than usual; but taken in connection with the other agreeing observations, they help to establish the fact that pyrosulphuryl chloride is one of the two products of the reaction. With pyrosulphuryl chloride established as one of the products, the table of analyses show beyond a doubt that the other is silicon oxychloride.

The more regulated action of water on the distillate was next studied in the effort to destroy one substance and isolate the other. In searching for a neutral diluant it was found that alcohol, acetone, benzol reacted with the distillate, but carbon tetrachloride, chloroform, and carbon disulphide did not; chloroform and carbon tetrachloride were used. 103 grams of chloroform were mixed with 84 grams of the distillate, the diluted material cooled to $-5°$ and water added drop by drop. Each drop caused the formation of a white ball which when pricked, burst with a slight explosion and formation of hydrochloric acid. The action evidently consisted in the coating of the entering drop with a silica shell; while on pricking, the unchanged water was freed and reacted further. 3 grams of water were added, approximately the amount required to change all the pyrosulphuryl chloride present to chlorsulphonic acid. On transferring the material a sediment of 6.5 grams (silica) was found. A distillation at low pressure removed the chloroform and hydrochloric acid; a distillate of 42 grams was collected, while a semi-solid residue was left in the boiling flask. A second distillation at low pressure gave 38 grams, free from hydrochloric acid. The density at 18° was 1.73 (pyrosulphuryl chloride is 1.837 at 20°). An analysis showed the change produced by the water:

		S	Si	Cl
(24)	Before treatment with water:	16.7%	—	49.9%
(21)	After " " "	20.1	6.1	43.4

The figures show that the water attacked mainly the silicon body. A treatment with salt followed and the distillate from the salt mixture was collected, under diminished pressure, in two fractions: the lower one, 9 grams, between 50° and 110°, with oil-bath around the boiling flask raised to 150°; the second, 4.5 grams, with the bath heated to

210°, the pressure being 20 mm. throughout. The analyses resulted as follows:

		S	Si	Cl
(22)	9 grams	19.9%	6.75%	43.4%
(23)	4.5 grams	24.2	3.9	35.2
For comparison, $S_2O_5Cl_2$		29.82	—	32.98

The figures for the 9 grams indicate that no appreciable amount of chlorsulphonic acid had been removed, hence that the water treatment destroyed the silicon body, and yielded the sulphur containing body. That this sulphur body is pyrosulphuryl chloride is indicated by the figures for the 4.5 grams obtained by heating the salt residue to a temperature exceeding 200°, while the pressure was kept at 20 mm.

In another preparation in which hydrous sulphur trioxide was used of such a strength that there was enough water present to form chlorsulphonic acid instead of pyrosulphuryl chloride according to the reaction: $2SO_3 + H_2O + SiCl_4 = 2ClSO_3H + SiOCl_2$, that acid was indeed obtained, but the reaction had taken place in a different way. The water decomposed a portion of the silicon tetrachloride, forming silica to such an extent that the solid residue in the flask after distillation was 50 percent by weight of the materials taken, and hydrochloric acid, which combined with the sulphur trioxide to form chlorsulphonic acid, a portion of the silicon tetrachloride was recovered unchanged in the liquid air condenser; all the silicon not accounted for by it was present in the solid residue.

Three preparations have been observed which approached pyrosulphuryl chloride. The most nearly pure was obtained early in our work by distilling a homogeneous mixture of 115 grams of 94 percent sulphur trioxide and 111 grams of silicon tetrachloride (2 molecules to 1) resulting after 12 hours' shaking at room temperature. A large amount of gelatinous silica was filtered off through glass wool, and the 144 grams of filtrate submitted to a distillation at low pressure; the distillate was collected in four fractions; the analysis of the first one, boiling at 60° to 100° with a pressure of 70 mm., has been given under (20) in the table of analyses; the last, boiled at 105°, with the oil-bath surrounding the flask 240°, and pressure 60 mm., accompanied by violent foaming, and left a solid residue of 50 grams; its analysis follows:

	S	Si	Cl
Found	28%	0.17%	29.4%
$S_2O_5Cl_2$	29.82	—	32.98

The experiment on the action of water on the average distillate diluted by chloroform has been recorded; there too on heating to 210°

with a pressure of 20 mm. and leaving a solid residue mainly sodium chloride in the flask, a last fraction of 4.5 grams rich in pyrosulphuryl chloride was obtained, as shown by its analysis (23) and behavior with water. In the third case 197 grams of a liquid prepared just like the 144 grams above, and not previously distilled, were mixed with the 116 grams of phosphorus pentoxide and distilled at low pressure; only 38 grams could be collected, in three fractions, with the bath surrounding the flask at 220°. On attempting to heat with the free flame, because the distillate came at the rate of a drop per minute, the flask exploded. These fractions were tested as to their melting-point; they all solidified readily in large crystals, radiating from one point, exactly as pyrosulphuryl chloride does; the first and second melted at near −40°, the third near −50°; pyrosulphuryl chloride melts at −37°; one of the fractions was tested for silica and contained none. It would seem as if by distilling from any solid, so that a high temperature is required, the silicon body is destroyed, while the more resisting pyrosulphuryl chloride can be collected.

That no chlorsulphonic acid was present in our original distillate was proved by an experiment performed in our first extended study and already recorded. See page 584.

In an attempt to obtain the ethyl ester of the silicon containing body,[19] the material diluted by carbon tetrachloride was treated with alcohol and after distilling off the solvent there remained in the boiling flask a semi-solid mass which was silica and ethyl sulphuric acid. The experiment was repeated several times, always with the same result. That the ethyl ester of silicon oxychloride was not obtained does not show the absence of silicon oxychloride, for such an ester would hardly be stable in presence of ethyl sulphuric acid and other products of water on pyrosulphuryl chloride.

An examination of the table of complete analyses shows that different specimens of the distillate contain the pyrosulphuryl chloride and silicon oxychloride in different proportions, three of them show percentages approaching those required if the two substances are present in molecular proportions.

	S	Si	Cl
Calculated for $S_2O_5Cl_2 + Si_2OCl_6$	12.82%	11.31%	56.59%
(2)	14.63	10.20	54.87
(19)	15.14	10.14	53.15
(1)	16.9	9.4	53.3

[19] Friedel and Ladenburg prepared the ethyl ester of silicon oxychloride $(C_2H_5)_6OSi_2$; reference 5. Compare Friedel and Crafts, Ann. Chim. phys. **9**, 12 (1886); Ladenburg, Lieb. Ann., **173**, 144 (1874).

Besides these, several incomplete analyses show similar proportions:

	S	Si	Cl
(3)	14.50	10.18	—
(24)	16.7	—	49.9
(26)	15.3	—	50.6

The results leave much to be desired but certainly indicate that the two products were formed approximately in the proportions required by the reaction:

$$2SO_3 + 2SiCl_4 = S_2O_5Cl_2 + Si_2OCl_6 \qquad (1)$$

In the majority of analyses percentages were found indicating a decided excess of pyrosulphuryl chloride, and a smaller proportion of silicon oxychloride; the silicon varying from 7.75 to 3.7, instead of being 11.31; the sulphur varied from 19.6 to 24.28 instead of being 12.82. The formation of more pyrosulphuryl chloride, and the destruction of silicon oxychloride is accounted for by the reaction:

$$Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5Cl_2 \qquad (2)$$

An especially large percent of sulphur indicating a great excess of pyrosulphuryl chloride was obtained from a specimen which had stood 3 summer months undistilled, that is, with the low-boiling portions containing the excess of sulphur trioxide still unseparated from the higher boiling portions. It was contained in a glass-stoppered bottle under a bell-jar whose atmosphere was dried by phosphorus pentoxide. Comparing this material with a similar one, which had been heated for 6 hours and had not stood at all, it was found that the higher boiling fraction had increased on standing from 3 percent to 38 percent, the solid deposited rising at the same time from 2.3 percent to 23 percent; in another more favorable case the figures for a similar mixture heated for 6 hours were 15 percent of higher boiling fraction, and 8 percent solid. In all three cases two molecules of sulphur trioxide had been used to each molecule of the silicon tetrachloride. Reaction (1) calls for equal molecules of the two, while (2) requires six molecules of the trioxide to each one of the oxychloride already formed, but no more silicon tetrachloride. This action should be reflected in the lower boiling fraction in an increase in the proportion of silicon tetrachloride, evidenced by a higher percentage of chlorine; an analysis showed that it contained, in the case of the material which stood 3 months, 65.5 percent of chlorine, whereas the original mixture of silicon tetrachloride and sulphur trioxide contained only 42.95 percent; this shows that the action is correctly interpreted by reaction (2). It is

important to add that once the higher boiling fraction was removed from the excess of sulphur trioxide, or which is the same, from the low-boiling fraction, no solid was deposited.

Most of the mixtures of pyrosulphuryl chloride and silicon oxychloride obtained by us crystallized at various temperatures, the highest one being $-60°$, the lowest $-78°$; some of them did not crystallize, but merely solidified to a vitreous mass, near $-120°$. Pyrosulphuryl chloride melts at $-37°$, silicon oxychloride near $-40°$. A mixture of equal parts of the prepared pure substances melted at $-40°$ to $-38°$, but on mixing 15.6 grams of the former with 5.2 grams of the latter, and heating half of the mixture on the Bunsen flame, it was found that the heated portion took twenty times longer to crystallize than the unheated one. As stated in the introduction, the only possible explanation is that the two substances form a compound under the influence of heat. All the mixtures were obtained by means of one or more distillations, and submitted to the heat of a flame, and this influence of heat explains the phenomena of crystallization observed. In the mixtures containing approximately one molecule of each substance, the two substances are combined, and not being free, cannot crystallize when a seed of either substance is introduced; in the mixtures containing an excess of pyrosulphuryl chloride, the silicon oxychloride is all combined, but some of the pyrosulphuryl chloride remains free, hence this mixture can crystallize on a seed of pyrosulphuryl chloride, although here again, it will not crystallize on a seed of the oxychloride.

The deposit formed on standing over the summer was placed in a Gooch crucible, washed twice with silicon tetrachloride, pressing down the material with a glass rod, and using a suction pump to remove all the liquid: all as rapidly as possible. The solid was then packed and sealed in tubes, in which it remained without alteration. This material appears perfectly dry; it smokes strongly in the air and attracts moisture rapidly. With water it reacts violently; a few bubbles of gas escape, and a slight yellow color (due to chlorine) develops; the white particles become transparent, but retain their original shape; no visible amount of silica separates out from the liquid. The reaction with dilute sodium hydroxide is the same, but more violent. When moistened with chloroform the solid becomes translucent and filled with bubbles. Heated over the flame it evolves white fumes, and leaves behind a white ash, which no longer reacts with water. The deposit is not homogeneous; the silicon percentage varied between 6 and 10; the portions which had been formed against the wall of the flask contained the higher percentage. One sample contained:

S	Cl	Si
26.8%	18.3%	6.2%

The study of this solid suggests that it is silica enclosing much sulphur trioxide and some silicon oxychloride and pyrosulphuryl chloride. This silica would have been formed by the equation, which has been discussed before,

$$Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5Cl_2$$

Our reasons for contending that silico-phosgene is not formed have been fully stated in the introduction.

SUMMARY.

Melted sulphur trioxide and silicon tetrachloride are miscible; on standing a long time or on heating 6 to 10 hours to 50° a reaction takes place:

$$2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2;$$

an excess of sulphur trioxide causes a further reaction:

$$Si_2OCl_6 + 6SO_3 = SiO_2 + 3S_2O_5Cl_2$$

The most significant result, as regards the relation of carbon and silicon, is the non-formation of silico-phosgene.

We take pleasure in acknowledging a grant from the Cyrus M. Warren Fund of Harvard University, with which the expense for the liquid air was met.

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